

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7:		A61L 15/00, 15/28	
(52) International Application Number:		PCT/NL99/00776	
(53) International Filing Date:		16 December 1999 (16.12.99)	
(54) Priority Date:		16 December 1998 (16.12.98)	
(55) International Publication Number:		WO 00/35304	
(56) Agent:		DE BRUIN, Leonard, C. et al.; Nederlandse Organisatie, Scheveningseweg 82, P.O. Box 29720, NL-2500 LB The Hague (NL).	
(57) Abstract:		<p>(71) Applicant (for all designated States except US): SCA HY-CHENS PRODUITS ZEST B.V. [NL/NL]; P.O. Box 360, NL-3700 AJ Zaan (NL).</p> <p>(72) Inventors and (73) Invented Agents (for US only): THORNTON, Jeffrey, [US/NL]; 13, NL-1272 AC Rivecourt-GM, SCHELVEN, [NL/NL]; Zandweg 12A, NL-0541 NR Nibmegen (NL); THORNTON, Helen, [NL/NL]; Nico Bergsteinsweg 147, NL-3931 CC Woudenberg (NL); VAN BRUNSEL-VERRAEST, Dorothea, [NL/NL]; Koppeld I, NL-2411 WO Bodegraven (NL); BIEBERG, Luca [IT/EE]; Torggatan 12 Apt. 348, S-411 37 Odenburg (SE); VAN DER VEG, [NL/NL]; 11, NL-3720 SR Vianen (NL); VAN DER VEG, [NL/NL]; 23A, NL-3704 BJ Zaan (NL); BIEBERG, [NL/NL]; Breg. Br. H. v.d. Boschstraat 111, NL-3938</p>	

(54) Title: ACIDIC SUPERABSORBENT POLYSACCHARIDES

(57) Abstract:

A process is disclosed for producing an acidic superabsorbent polysaccharide derivative, comprising the steps of: (a) crosslinking at least one polysaccharide containing acidic groups, such as carboxymethyl cellulose under 6-carboxy anhydride, with a crosslinking agent to produce a gel; (b) adjusting the pH of the polysaccharide to a value between 3.5 and 5.5; (c) comminuting the swollen polysaccharide into particles; and (d) drying the particles to produce the superabsorbent polysaccharide derivative. The process has a pH before 3 and provides color control when contacted with malodorous fluids.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LA	Laos	SI	Slovenia
AM	Armenia	FI	Finland	LB	Lebanon	SK	Slovakia
AO	Angola	FR	France	LY	Libya	SL	Serbia
AT	Austria	GB	Great Britain	LV	Latvia	SM	San Marino
AU	Australia	GR	Greece	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GU	Guam	MD	Moldova	TO	Togo
BB	Barbados	HN	Honduras	MO	Macao	TR	Turkey
BE	Belgium	IE	Ireland	MP	Marshall Islands	TT	Trinidad and Tobago
BF	Burkina Faso	IL	Israel	MT	Malta	UA	Ukraine
BG	Bulgaria	IT	Italy	NE	Niger	UG	Uganda
BR	Brazil	JP	Japan	NL	Netherlands	US	United States of America
BS	Bahamas	KE	Kenya	NO	Norway	VN	Viet Nam
BT	Bhutan	KZ	Kazakhstan	PL	Poland	YU	Yugoslavia
BZ	Belize	KR	Republic of Korea	PT	Portugal	ZW	Zimbabwe
CA	Canada	KW	Kuwait	RO	Romania		
CC	Cocos (Keeling) Islands	KG	Kyrgyzstan	RU	Russian Federation		
CF	Cote d'Ivoire	LA	Laos	SD	Sudan		
CG	Congo	LB	Lebanon	SE	Sweden		
CH	Switzerland	LC	St. Lucia	SG	Singapore		
CI	Cote d'Ivoire	LI	Liechtenstein				
CL	Chile	LK	Sri Lanka				
CM	Cameroun	LR	Liberia				
CN	China						
CO	Colombia						
CU	Cuba						
CV	Cape Verde						
CX	Christmas Island						
CY	Cyprus						
CZ	Czech Republic						
DE	Germany						
DK	Denmark						

Acidic superabsorbent polysaccharides

[0001] The present invention relates to a superabsorbent material which has enhanced odour control and prevents bacterial growth, based on polysaccharides, and to a method of producing such material.

[0002] Superabsorbent materials of various types are known in the art. Examples are crosslinked polyacrylates and polysaccharides grafted with polyacrylates. A problem related to the use of superabsorbent materials is the odour caused by urine components which cause superabsorbent materials to become objectionable long before their maximum absorbing capacity has been used. Furthermore, the known absorbent materials are normally based on non-removable and/or non-biodegradable raw materials. Consequently, there is a need for superabsorbent materials, which have odour control and reduced bacterial growth when contacted with body fluids, and which are biodegradable.

[0003] W/O 98/27117 discloses a superabsorbent polysaccharide derivative obtained by oxidation and crosslinking of a polysaccharide such as starch, in which at least 0.1 carbonyl group per monosaccharide unit of the polysaccharide derivative has been oxidised to a carboxyl group, the total number of carboxyl groups per monosaccharide unit being 0.2-3.0, and the derivative results from reaction with at least 0.001 equivalent of crosslinking agent per monosaccharide unit. The derivatives are not devised for odour control. US 5,247,072 describes superabsorbent carboxyalkyl polysaccharides, especially carboxymethyl cellulose, without odour control, obtained by crosslinking as a result of heat treatment. EP-A-202127 discloses superabsorbent articles for reducing diaper rash, which contain acid in distinct zones to control the skin pH between 3.0 and 5.5.

[0004] It has been found that a superabsorbent polymer with improved odour control can be produced by a process comprising the steps of:

- (a) crosslinking at least one polysaccharide containing acidic groups with a crosslinking agent to produce a gel;
 - (b) ensuring that pH of the polysaccharide is between 3.5 and 5.5 and, if necessary, adjusting the pH to between 3.5 and 5.5, especially to between 3.9 and 4.9;
 - (c) comminuting the acidified polysaccharide gel; and
 - (d) drying the comminuted polysaccharide at elevated temperature.
- [0005] The term "polysaccharide containing acidic groups" is understood to comprise polysaccharides having a pK of less than 5, down to about 1.5. Such polysaccharides may

contain carboxylic groups, sulphonic groups $(-O-SO_3-OH)$, phosphonic groups $(-O-PO(OH)_2)$, ammonium groups $(-NR_3H^+)$, wherein R is alkyl or hydrogen) and combinations thereof. The carboxylic groups may be present as a result of carboxylation, in particular carboxymethylation, or as a result of reaction with an anhydride such as maleic or succinic anhydride or as a result of oxidation, e.g. of a hydroxymethyl group $(-CH_2OH)$, usually at C6 of a monosaccharide unit), or of a bis(hydroxymethyl) group $(-CHOH-CHOH-$, usually at C2-C3 of a monosaccharide unit).

[0006] The phosphonic groups may be present as phosphate groups, resulting e.g. from reaction with phosphorylating agents (see e.g. W/O 97/28298), or as phosphonic or phosphinic acid groups, resulting e.g. from reaction with halomethyl phosphonic acids. The sulphonic acids may be present e.g. as sulphate groups or as a result of sulphate addition to polysaccharide aldehydes (see e.g. W/O 99/29354) or to maleic anhydride adducts (products with $-O-CO-CH_2-CH(COOH)-SO_3H$ groups). The ammonium groups are also acidic groups, and can result from protonation of amine groups, such as in chitosan-type polysaccharides or in aminoalkylated polysaccharides.

[0007] The polysaccharides may be α -glucans like starch, amylose and amylopectin, β -glucans like cellulose and cellobiose, galactomannans like guar gum (guaran) and locust bean gum, galactomannans including e.g. xanthan gum, fructans, (arabino)xylans, galactans including alginates and pectin and other mixed polysaccharides. Starch and cellulose are particularly preferred. Starch may be derived from any suitable source, such as corn, wheat, potato, rice and the like; it may also be a residual, crude or lower-grade starch product containing minor amounts of other biopolymers such as cellulose, pectin or protein. Cellulose may also contain minor amounts of other materials such as hemicellulose.

[0008] The polysaccharides may comprise non-ionic, non-carboxylated derivatives such as hydroxyalkyl polysaccharides, but the presence of such non-ionic derivatives does not have a particular advantage. The chain length of the polysaccharides is important although there is no critical minimum for the molecular weight. In general, polysaccharides having a molecular weight of more than 1,000 are preferred. A molecular weight above about 25,000 may have a positive effect on the properties of the oxidised product.

[0009] The acidic polysaccharide can be a carboxymethyl polysaccharide without further substitution, such as carboxymethyl cellulose, preferably having a degree of substitution of 0.3-3.0, more preferably 0.5-1.5. For such carboxymethylated polysaccharides, the process advantageously comprises the further step of contacting the crosslinked polysaccharide with an organic solvent which is at least partly miscible with water, between step (b) and step (c).

The organic solvent is preferably a water-miscible alcohol such as methanol, ethanol, methoxyethanol or isopropanol, a water-miscible ether such as dioxane, tetrahydrofuran or dimethoxyethane, or a water-miscible ketone, such as acetone. Most preferred are methanol and ethanol. The amount of solvent can be e.g. 2-30 times the amount of the gelled polysaccharide. The water-miscible solvent is evaporated before or during step (d).

[0010] The carboxymethylated polysaccharide can also be a carboxymethyl polysaccharide containing further carboxyl groups produced by oxidation of asaccharide carbinol groups. Such carboxyl groups may be 2- and/or 3-carboxyl groups obtained by oxidation of anhydroglyucose rings of the polysaccharide using hypochlorite or periodate/chlorite, but preferably they are 6-carboxyl groups obtained by oxidation of the 6-hydroxymethyl group, e.g. with a nitroxyl compound (TEMPO) as a catalyst. In such carboxy-carboxymethyl polysaccharide, such as 6-carboxy-carboxymethyl starch or 6-carboxy-carboxymethyl-cellulose, the degree of substitution for carboxymethyl is preferably 0.2-0.8, especially 0.3-0.6, and the degree of substitution for 6-carboxyl groups is preferably 0.1-0.5, more preferably 0.15-0.4.

[0011] Suitable oxidation methods are described in WO 98/27117 and references cited therein. TEMPO oxidation may be performed with hypochlorite with or without bromide as a catalyst, or with peracid/bromide or another oxidant. Unsubstituted TEMPO or 4-hydroxy or 4-acetamido-TEMPO or mixtures thereof may be used. When oxidations resulting in salt production are used, the salts may advantageously be removed after the oxidation reaction.

[0012] Similarly, the acidic polysaccharide may contain both other acidic groups obtained by substitution, and carboxyl groups obtained by oxidation. Such other acidic groups obtained by oxidation include e.g. phosphonic groups obtained by phosphorylation of the polysaccharide, sulphonyl groups and carboxyalkylcarbonyl groups obtained by reaction with a dicarboxylic anhydride. Substitution and oxidation may be performed in either order, e.g. first phosphorylation and then oxidation, or first oxidation and then phosphorylation. Combinations of different acidic substituents e.g. carboxyalkyl groups and phosphonic groups are also suitable.

[0013] In such oxidised and substituted (carboxyalkyl or other) polysaccharides the addition of an organic water-miscible solvent can be dispensed with, as a gel with the required structure already results from direct cross-linking.

[0014] The polysaccharide containing acidic groups can also be a carboxylated polysaccharide wherein the carboxyl groups have been introduced by oxidation of asaccharide carbinol groups in a manner as described above, without carboxyalkylation. Such oxidised polysaccharides include dicarboxy polysaccharides (obtained by C2-C3 oxidation) and,

especially 6-carboxy polysaccharides, e.g. obtained by TEMPO oxidation, especially 6-carboxy starch. These polysaccharides do not require the use of a water-miscible solvent after crosslinking.

[0015] The polysaccharide containing acidic groups may also be a mixture of acidic polysaccharides as described above. A particularly useful mixture is a mixture of carboxymethyl cellulose and 6-carboxy starch, e.g. in a ratio of between 1:1 and 1:20. Other mixtures are also quite useful, e.g. carboxymethyl cellulose and carboxymethyl starch, or carboxymethyl starch and cellulose phosphate having a degree of substitution of about 0.3 to about 0.5.

[0016] The polysaccharide containing acidic groups is reacted with a crosslinking agent to produce a gel. A gel is defined herein as a polymeric network based on polysaccharides, which swells in water and does not dissolve in water. Crosslinking agents are reagents containing two or more functions capable of reacting with a hydroxyl group, resulting in intra- and inter-molecular bonds between different mono-saccharide units. Suitable crosslinking agents may act on the hydroxyl groups of different polysaccharide chains and include divinyl sulphone, epichlorohydrin, diepoxybutane, diglycidyl ethers, diisocyanates, cyanuric chloride, trimetaphosphates, phosphoryl chloride, and mixed anhydrides, and also inorganic crosslinkers such as aluminium and zirconium ions, but are not restricted to these examples. Mixtures of crosslinkers may also be used.

[0017] Especially preferred crosslinkers, in particular for crosslinking at elevated temperature and/or concentration, are crosslinkers that are active under neutral or acidic conditions, such as bis-epoxy crosslinkers, for example diepoxybutane, 1,5-diepoxyhexane, 1,7-diepoxyoctane, bis-glycidyl ether, glycol bis-glycidyl ether, butanediol bis-glycidyl ether and the like, as well as mixtures of different crosslinkers. Crosslinking can also be performed using carboxyl or aldehyde groups formed by oxidation or carboxyl groups introduced by carboxyalkylation, e.g. using polyols, polyamines or other polyfunctional reagents. Esterification and other crosslinking methods described herein can also be effected intramolecularly at the surface between the carboxyl group of one polysaccharide chain and a hydroxyl group of another chain as known in the art. This inter-chain crosslinking can be catalysed by an acid or a multivalent ion such as magnesium or calcium, or by heating. Divinyl sulphone is another preferred crosslinker. Crosslinking of starch and other polysaccharides is well-known in the art. A description of crosslinking agents and reaction conditions can be found e.g. in "Starch Derivatives: Production and Uses" by M.W. Rutenberg and D. Solarek, Acad. Press Inc., 1984, pages 324-332.

[0018] According to a preferred embodiment of the invention, crosslinking is performed

under conditions of increased temperatures and high concentrations. The temperatures are typically at least 100°C, more preferably between 120 and 180°C. The concentration of the polysaccharide to be crosslinked is at least 20 % by weight, more particularly between 25 and 65 % by weight with respect to the total aqueous crosslinking mixture. The crosslinking mixture may further contain a plasticiser such as a polyol. Suitable polyol plasticisers include glycerol, ethylene glycol, propylene glycol, polyethylene glycol, polypropylene glycol, glycol and glycerol monoesters, sorbitol, mannitol, monosaccharides, citric acid monoesters and the like. The amount of plasticiser may vary from 1 to 25 % weight of the crosslinking mixture. The crosslinking can be conveniently performed in a kneading apparatus or an extruder under conditions of reactive processing. The various components of the crosslinking mixture can be mixed before entering the extruder, or one or more of them, e.g. the crosslinking agent, may be added at a later stage in the extruder.

[0019] After crosslinking, the crosslinked polysaccharide is treated with an acid so as to reduce the pH to 3.5 to 5.5. However, if the crosslinking is performed under acidic conditions, such as with bis-epoxy crosslinkers, the acidification takes place before crosslinking, and an adjustment of a pH to between 3.5 and 5.5 may or may not be needed after the crosslinking step. Suitable acidifying reagents include inorganic and organic acids such as hydrochloric, phosphoric, acetic acid etc. If crosslinking is performed under normal conditions (ambient temperature or up to about 100°C, atmospheric pressure, lower concentration) or before acidification, it is preferred that the polysaccharide is acidified to pH 4.9 or lower. After acidification, the cross-linked, gel-like material is comminuted to smaller particles, e.g. in the range of 0.5-5 mm.

[0020] Instead of or in addition to the treatment with the water-miscible organic solvent described above, an additional post-crosslinking step (surface crosslinking) may be applied to strengthen the gel. This post-crosslinking may be performed after the comminuting step c or even after the drying step d, resulting in different swelling degrees of the gel particles obtained. The crosslinking agent to be used in this post-crosslinking step can be the same as those referred to above for the first crosslinking step. In this procedure, the gel particles are slightly swollen, and treated and mixed with a crosslinking agent, and subsequently the particles are dried at a temperature which depends on the liquid used to swell the gel particles and on the crosslinking agent. The post-crosslinking may be performed in the presence of compounds providing further crosslinks at the outside of the gel particle. Such compounds may include bifunctional or multifunctional capable of reacting with hydroxyl and (if still present) carboxyl functions, for example diamines, polyamines, polyamide-

amine-epichlorohydrin (PAE resin), bis-epoxy compounds, chitosan-like compounds, metal salts (zincium, aluminium), dialdehydes, or polyaldehyde-polycarboxy starch derivatives.

[0021] The comminuted material is dried, preferably in a fluidised bed drier. Drying can be performed at ambient temperatures, but preferably increased temperatures are used, in particular above 50°C, more in particular above 70°C. Drying times from 15 minutes up to 8 hours or more can be applied. Preferably an additional heat treatment is performed after the initial (fluidised bed) drying; this additional drying step can be performed at 80-150°C, e.g. for 2 minutes to 2 hours, and results in a further enhanced gel strength of the product.

[0022] The invention also pertains to a bacteriologically stable superabsorbent polysaccharide derivative having odour control of absorbed liquid, as well as to a superabsorbent article in which this derivative is incorporated. The derivative and the article preferably have a pH below 5 (down to 3.5) when contacted with neutral or near-neutral water; if necessary, an acidifying agent can be incorporated in a sufficient amount to maintain the required low pH. Suitable acidifying agents include organic di- or poly-carboxylic acids such as citric, maleic, fumaric, oxalic, malonic, succinic, tartaric and similar acids, hydroxyacids such as gluconic, ascorbic, glycolic, glyceric, lactic, salicylic acid and the like, as well as benzoic acid and phosphoric and other inorganic acids. These acids may be used in combination with their partially neutralised salts (e.g. monosodium citrate or monopotassium phosphate) to provide buffering capacity. Also, neutral materials such as acid anhydrides and lactones, e.g. maleic anhydride, succinic anhydride, β -gluconolactone, can be incorporated for lowering the pH.

[0023] The superabsorbent polysaccharides combine high absorption capacity with control of bacterial growth and control of odour, as well as with biodegradability. The absorption capacity can be expressed as free swelling capacity (FSC) and the centrifugal retention capacity (CRC), and with the absorption under load (AUL), using synthetic urine (SU) as test liquid. The composition of the synthetic urine is as follows: 300 mM urea, 60 mM KCl, 130 mM NaCl, 2.0 mM $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, 3.5 mM MgSO_4 , and 1 mg/l Triton X-100 in deionised water.

[0024] The superabsorbent polysaccharide derivatives of the invention can be used for absorbing liquids, especially of body fluids which contain various salts and non-ionic substances. The product is particularly suitable for the production of absorbent hygiene articles, such as diapers, sanitary napkins and the like. Such articles can be produced entirely on the basis of the polysaccharides according to the invention, but they can also contain conventional absorbent materials, such as cellulose pulp in addition to the absorbents

according to the invention. The absorbent article is preferably part of a layered product, in which the superabsorbent polymer constitutes at least one layer. The absorbent layer can be located between a liquid-permeous top layer and a liquid-impermeous bottom layer. In particular the product may have four layers. The first one can be a thin, non-woven layer of polyester fibres or other fibres. The second layer can be a wadding which is used for acquiring and spreading the absorbed fluid such as urine. The third layer can consist of fluff pulp wherein the SAP is spread as fine particles, especially 50-800 µm. The last layer can be a back sheet of a water-resistant material such as polyethylene, which prevents leakage from the layered absorption product.

10

Example 1: Absorbent 6-carboxy-carboxymethyl potato starch

[0025] Carboxymethyl starch (degree of substitution 0.5) derived from potato starch was converted to 6-carboxy carboxymethyl starch by TEMPO-catalysed oxidation (degree of oxidation 0.25). A 20% aqueous solution of the product was cross-linked with different amounts of divinyl sulphone (0.5, 0.6, 0.7 mol% DVS). After 15 hours, an insoluble network was formed. The gel was brought into distilled water and allowed to swell. The pH of the material was lowered to pH 4.1 by controlled addition of 1M HCl. After equilibration, the gel was filtrated and dried in a fluidised bed drier at 70°C. The following absorption characteristics (FSC, CRC, AUL at 2.0 kPa) measured in synthetic urine (SU) were obtained:

20

Cross-linking degree (mol% DVS)	FSC (g/g)	CRC (g/g)	AUL (g/g) 2 kPa	pH gel
0.5	31	19	12	4.1
0.6	30	18	14	4.1
0.7	27.5	17	18.5	4.1

Example 2: Absorbent 6-carboxy-carboxymethyl high amylose corn starch

[0026] Carboxymethyl starch (degree of substitution 0.53) derived from high amylose corn starch was converted to 6-carboxy carboxymethyl starch by TEMPO-analysed oxidation (degree of oxidation 0.09). A 20% aqueous solution of the product was cross-linked with different amounts of divinyl sulphone (1.0, 1.5, 2.0, 2.5 mol% DVS). After 16 hours, an insoluble network was formed. The gel was brought into distilled water and allowed to swell. The pH of the material was lowered to about pH 4.1 by controlled addition of 1M HCl. After equilibration, the gel was filtrated and dried in a fluidised bed drier at 80°C. The

25

above table summarises the absorption characteristics (FSC, CRC, AUL) measured in synthetic urine (SU) as obtained.

Cross-linking degree (mol% DVS)	FSC (g/g)	CRC (g/g)	AUL (g/g) 2 kPa	pH gel
1.0	29.5	20	17	4.0
1.5	34.5	20.5	13	4.1
2.0	33.0	18	16	4.3
2.5	28.5	16	17	4.0

Example 3: Absorbent carboxymethyl cellulose treated with methanol

DXL ¹	XL reaction ² cond. (°C/h)	FBD (°C/min)	FSC (g/g)	CRC (g/g)	AUL (g/g)
10	20°/20h ³	100°/10m	29	11	17
10	20°/20h	100°/10m	34	16	22
10	80°/2h	100°/10m	38	18	20
20	50°/8h	100°/10m	19.5	6.5	14
10	50°/8h	100°/10m	28.5	12	19.5
5	50°/8h	100°/10m	31.5	15	20.5
5	50°/15h	100°/15m	34.5	18	23
5	50°/15h	80°/15m	40	19.5	21
5	50°/15h	60°/15m	34	15.5	20
5	50°/15h	40°/30m	33	15	18.5

¹: degree of crosslinking used, (mol% BDDE)

²: crosslinking reaction

³: pH controlled by acetic acid instead of HCl.

10

[0027] A 2 wt% aqueous solution of CMC (Cekol 50,000 from Metasa Specialty Chemicals, degree of substitution 0.8) was prepared and the pH was adjusted to 4.0 by slow addition of HCl under stirring (alternatively, glacial acetic acid can be used according to WO 86/09912, example 2b). The required amount of a 10 or 20 vol.% aqueous solution of 1,4-butanediol diglycidyl ether (BDDE) was added and the reaction mixture was thoroughly mixed. The gel obtained was cut into pieces and suspended overnight in a fivefold excess of

15

methanol). The methanol was filtered out and the gel was milled in a blender, and the particles were dried in a fluidised bed drier (FBD). The dried product was ground in a mortar. The absorption characteristics for synthetic urine (SU) are summarised in the table above, with details on crosslinking and drying.

Example 4: Absorbent carboxymethyl cellulose treated with methanol

[0028] A 2 wt% solution of CMC (Cekol 50,000 from Metas Specialty Chemicals, degree of substitution 0.8) in 0.05 M aqueous NaOH was reacted with 14 mol% of DVS for 18 hours at room temperature. The gel obtained was chopped in pieces of roughly 3-4 cm and the pieces were brought in a fivefold excess of methanol. The gel was then acidified using 1M HCl to a pH varying from 4.4 to 4.0. After about 24 h the swollen gel was milled in a blender to obtain smaller particles, and then put back in the methanol for another 24 h to achieve homogeneous acidification of the gel material. Thereafter ground particles were dried in a fluidised bed drier at 100°C for 30 min, and then further heat-treated at 120°C in an oven for about 30 min. The absorption characteristics for SU are summarised in the following table.

amount of acid added (m)	pH gel	before thermal treatment			After thermal treatment		
		FSC (g/g)	CRC (g/g)	AUL (g/g)	FSC (g/g)	CRC (g/g)	AUL (g/g)
28	4.4	83	64	10	40	26	17
30	4.2	57	42	12	29	17	16.5
33	4.0	55	41	13	28	15	16
35	4.0	39	26	13	21	11	15

Example 5: Absorbent carboxymethyl cellulose treated with ethanol

[0029] Ten grams of CMC (Cekol 50,000) were dissolved in 500 ml NaOH (0.05 mol/l). At room temperature 0.62 ml DVS (4 mol%) was added under stirring. After 18 hours the crosslinked gel (450 g) was chopped into pieces and 28 ml of 1 mol/l HCl was added and thoroughly mixed to decrease the pH of the gel to 4.4. After 1 h 1400 ml of ethanol was added. After one week, the precipitated gel was ground with a blender and dried in an FBD for 30 minutes at 100°C. The dry particles were milled and sieved to obtain a final particle size of 100-800 µm. The following absorption characteristics (FSC, CRC, AUL) measured in synthetic urine were obtained: FSC: 132 g/g; CRC: 111 g/g; AUL: 11 g/g; pH gel 4.4.

Example 5a: Absorbent carboxymethyl cellulose treated with ethanol

[0030] In addition to the sample of example 5, a heat treatment was applied for 30 minutes at 120°C in an oven to improve the gel strength (AUL). The following absorption characteristics measured in synthetic urine were obtained: FSC: 52 g/g; CRC: 37 g/g; AUL: 17 g/g; pH gel 4.5.

Example 6: Absorbent carboxymethyl cellulose treated with ethanol

[0031] Ten grams of CMC (Cekol 50,000, DS 0.8) were dissolved in 500 ml water and 8.5 ml 1 mol/l HCl (pH 4.4). Then 1.27 ml of 20 % (v/v) BDDE in water (3 mol%) was added with stirring. After 8 hours at 50°C, the crosslinked gel was suspended in a threefold volume of ethanol with stirring. After one week, the precipitated gel was ground into small pieces with a blender and dried in a FBD for 15 minutes at 100°C. The dry particles were milled and sieved to obtain a final particle size of 100-800 µm. The following absorption characteristics measured in synthetic urine were obtained: FSC: 21 g/g; CRC: 13 g/g; AUL: 18 g/g; pH gel 4.3.

Example 7: Absorbent 6-carboxy starch/CMC crosslinked under alkaline conditions

[0032] Five g of TEMPO-oxidised starch (TOS, degree of oxidation 0.70) and 0.4 g of CMC (Cekol 50,000 from Metas Specialty Chemicals, degree of substitution 0.8) were dissolved in 20 ml of 0.05 M aqueous NaOH (pH 12) under mechanical stirring for 4 h. The mixture was crosslinked with 0.8 mol% of DVS (23 µl) at 5°C for 18 hours. Three g of the gel obtained was chopped in pieces and the pieces were brought in 600 ml of demi water and acidified with 1.8 ml of 1M HCl with mild stirring (stepwise addition of acid). The next day, the swollen gel was filtered over a 80 µm sieve, and brought in another 600 ml of demi water for half an hour. Subsequently the gel was dried in a fluidised bed drier at 80°C for 1 hour. The material was characterised in synthetic urine with the following results: 93% TOS / % CMC; FSC: 30 g/g; CRC: 17 g/g; AUL: 16.5 g/g; pH gel 4.6.

Example 8: Absorbent 6-carboxy starch/CMC crosslinked under acidic conditions

[0033] Five g of TEMPO-oxidised starch (TOS, degree of oxidation 0.70) and 0.4 g of CMC (Cekol 50,000 from Metas Specialty Chemicals, degree of substitution 0.8) were dissolved in 20 ml of demi water under mechanical stirring for 1 h. The pH was adjusted to 4.5 using 25% HCl. The mixture was crosslinked with 1.4 mol% of BDDE (1,4-butanediol

diglycidyl ether) (78 μ) at 50°C for 18 hours. The gel was chopped and the pieces were dried in a fluidised bed drier for 30 minutes at 100°C. The dried gel was ground and washed with excess demi water on a 80 μ m sieve to remove any salts present. Then the gel was dried in the fluidised bed drier at 80°C for 1 hour. The material was characterised in synthetic urine with the following results: 93% TOS / 7% CMC; FSC: 26 g/g; CRC: 15.5 g/g; AUL: 19 g/g; pH gel 4.9.

Example 9: Absorbent 6-carboxy starch crosslinked under acidic conditions

[0034] Five g of TEMPO-oxidised starch (TOS, degree of oxidation 0.70) was dissolved in 20 ml of demi water under mechanical stirring for 1 h. The pH was adjusted to 4.5 using 25% HCl. The mixture was crosslinked with 2.0 mol% of BDDE (113 μ) at 50°C for 18 hours. The gel was chopped and the pieces were dried in a fluidised bed drier for 30 minutes at 100°C. The dried gel was ground and washed with excess demi water on a 80 μ m sieve to remove any salts present. Then the gel was dried in the fluidised bed drier at 80°C for 1 hour. The material was characterised in synthetic urine with the following results: 100% TOS; FSC: 27 g/g; CRC: 16 g/g; AUL: 19 g/g; pH gel 4.8.

Example 10: Crosslinking of 6-carboxy starch by extrusion

[0035] In an extruder, 50 grams of 6-carboxy starch (0.25 mol) is mixed with 50 ml of a 0.3 M HCl solution containing 30 μ l butanediol diglycidyl ether (0.15 mmol). The paste is then extruded at 150°C with an average residence time of 1 minute in the extruder. At the extrusion die the crosslinked polysaccharide is chopped into small pieces. The small pieces of gel are then dried in a fluidised bed drier for 30 minutes at 100°C. The dried particles are ground and sieved to obtain a final particle size of 100-800 μ m. The absorption properties are comparable to those of the superabsorbent polysaccharide crosslinked in a conventional way.

Example 11: Absorbent 6-carboxy starch/CMC crosslinked under acidic conditions.

[0036] Three batches of 4 g of desalted TEMPO-oxidised starch (TOS, degree of oxidation 0.70) were dissolved in demi water to obtain 20wt%, 40wt% and 50wt% TOS solutions, respectively. The pH of the solutions was about 4.6. To the solutions 0.124 g of CMC (Cakol 50,000, degree of substitution 0.8) was added, followed by thorough mixing. The mixtures were crosslinked at 50 °C for 18 hours, with 1.4, 0.7, and 0.5 mol% of BDDE, respectively. Gels obtained were sized and, subsequently, dried in a fluidised bed

drier for 1 hour at 100 °C. The dried gels were ground and re-swollen in an excess of demi water. By addition of 2 M HCl, pH of the gel was adjusted to pH of 4.7-4.8 in demi water. Subsequently, the re-swollen gels were washed with excess demi water on a 80 μ m sieve to remove salts present. Then the gels were dried in the fluidised bed drier at 100 °C for 1 hour. The materials were characterised in synthetic urine with the following results for the 40% TOS material: DXL (= degree of crosslinking in mol% BDDE): 0.7; FSC: 26.5 g/g; CRC: 15.5 g/g; AUL 14 g/g; pH gel: 4.2. Comparable results were obtained when using 20% or 50% TOS solutions, instead of 40%.

Example 12: Absorbent 6-carboxy starch crosslinked under acidic conditions.

[0037] Three batches of 4 g of desalted TEMPO-oxidised starch (TOS, degree of oxidation 0.70) were dissolved in demi water to obtain 20wt%, 40wt% and 50wt% TOS solutions, respectively. The pH of the solutions was about 4.6. The solutions were cross-linked at 50 °C for 18 hours, with 2.0, 0.75, and 0.6 mol% of BDDE, respectively. Gels obtained were sized and, subsequently, dried in a fluidised bed drier for 1 hour at 100 °C. The dried gels were ground and re-swollen in an excess of demi water. By addition of 2 M HCl, pH of the gel was adjusted to pH of 4.7-4.8 in demi water. Subsequently, the re-swollen gels were washed with excess demi water on a 80 μ m sieve to remove salts present. Then the gels were dried in the fluidised bed drier at 100 °C for 1 hour. The materials were characterised in synthetic urine with the following results for the 40% TOS material: DXL 0.75; FSC: 28 g/g; CRC: 15 g/g; AUL 14 g/g; pH gel: 4.1. Comparable results were obtained when using 20% or 50% TOS solutions instead of 40%.

Example 13: Absorbent 6-carboxy starch/CMC crosslinked under acidic conditions

[0038] Three batches of 4 g of desalted TEMPO-oxidised starch (TOS, degree of oxidation 0.70) were dissolved in demi water to obtain 40wt% TOS-solutions. The pH of solutions was about 4.6. To each solution 0.124 g of CMC (Cakol 50,000, degree of substitution 0.8) was added, and the whole was mixed thoroughly. Mixtures were cross-linked with 0.7 mol% of BDDE at 50 °C for 18 hours, 70 °C for 2.5 hours, and 100 °C for 1 hour, respectively. Gels obtained were sized and, subsequently, dried in a fluidised bed drier for 1 hour at 100 °C. The dried gels were ground and re-swollen in an excess of demi water. By addition of 2 M HCl, pH of the gel was adjusted to pH of 4.7-4.8 in demi water. Subsequently, the re-swollen gels were washed with excess demi water on a 80 μ m sieve to remove any salts present. Then the gels were dried in the fluidised bed drier at

100 °C for 1 hour. The materials were characterised in synthetic urine with the following results:

5	XL temp. (°C)	XL time (h)	FSC (g/g)	CRC (g/g)	AUL (g/g)	pH gel
	50	18	26.5	15.5	14	4.2
	70	2.5	27	14	13	3.8
10	100	1	27	13.5	11.5	3.9

Example 14: Absorbent 6-carboxy starch crosslinked under acidic conditions.

[0039] Fifty g of desalted freeze-dried TEMPO-oxidised starch (TOS, degree of oxidation 0.70) was kneaded till a fibrous structure was obtained, and subsequently demi water (21.4 ml of demi water) was added. The whole was kneaded for 3 minutes at 17 °C to obtain 70 wt% TOS paste (pH of paste was ca. 4.6). To this paste 0.4 mol% BDDE was added and the whole was again kneaded for 3.5 minutes at 17 °C. Then the paste was crosslinked for 16 hours at 50 °C. The gel obtained was sized and dried in a fluidised bed drier for 1 hour at 80 °C. Dried gel particles were re-swollen in 10 liters of demi water, and subsequently dried in the fluidised bed drier for 1.5 hours at 80 °C. The material was characterised in synthetic urine with the following results: FSC: 27 g/g, CRC: 14.5 g/g, AUL: 17.5 g/g, pH gel 4.9.

Claims

1. A process of producing a superabsorbent polysaccharide derivative, comprising the steps of:
 - (a) crosslinking at least one polysaccharide containing acidic groups with a crosslinking agent to produce a gel;
 - (b) ensuring that the pH of the polysaccharide is between 3.5 and 5.5;
 - (c) comminuting the acidified polysaccharide gel; and
 - (d) drying the comminuted polysaccharide at elevated temperature.
2. A process according to claim 1, in which the polysaccharide containing acidic groups comprises carboxymethyl-cellulose, further comprising the step of contacting the crosslinked polysaccharide with an organic solvent which is at least partly miscible with water, between step (b) and step (c).
3. A process according to claim 2, in which said organic solvent is a lower alcohol, a water-miscible ketone or a water-miscible ether, especially methanol or ethanol.
4. A process according to claim 1, in which the polysaccharide containing acidic groups is a carboxymethyl polysaccharide further containing carboxyl groups resulting from oxidation of saccharidic hydroxymethyl or hydroxymethylene groups, or phosphonic or sulphonic acid groups.
5. A process according to claim 1, in which the polysaccharide containing acidic groups comprises a 6-carboxy polysaccharide, especially 6-carboxy starch, optionally mixed with a carboxymethylated polysaccharide.
6. A process according to any one of claims 1-5, in which the polysaccharide containing acidic groups contains 0.3-3.0 carboxyl groups per monosaccharide unit.
7. A process according to any one of claims 1-6, in which said cross-linking agent is a bis-epoxy compound, and the polysaccharide is acidified before step (a).

8. A process according to any one of claims 1-7, in which said crosslinking step is performed at a temperature of at least 100°C, preferably between 120 and 180 °C and/or at a concentration of the polysaccharide of between 25 and 75% by weight.

9. A process according to claim 8, in which a plasticiser such as glycerol is used during said crosslinking step.

10. A process according to any one of the preceding claims, in which said drying step (d) is performed using a fluidised bed, at a temperature of between 50 and 130°C.

11. A process according to any one of the preceding claims, in which said drying step (d) is followed by a heat treatment at a temperature of between 80 and 150°C.

12. A process according to any one of the preceding claims, in which an additional surface-crosslinking step is performed after step (c) or after step (d).

13. Superabsorbent polysaccharide derivative obtainable by the process according to any one of the preceding claims, and having a pH below 5.

14. Superabsorbent polysaccharide according to claim 13, also comprising an acid selected from organic di- and polycarboxylic acids, hydroxycarboxylic acids and benzoic acids.

15. Absorbent article comprising a superabsorbent polysaccharide according to claim 13 or 14.

INTERNATIONAL SEARCH REPORT

Int. Appl. No. PCT/NL 99/00776

CLASSIFICATION OF SUBJECT MATTER
IPC 7 A61L15/00 A61L15/28

According to International Patent Classification (IPC) or to both national classification and IPC

IPC 7 A61L15/00 A61L15/28

IPC 7 A61L15/00 A61L15/28

Documents mentioned other than prior art documents are indicated in the fields mentioned

Indicate the date when searched during the International search (name of date base used, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category * Choice of document, with indication, where appropriate, of the relevant passages

Relevant to date No.

X EP 0 644 207 A (NALCO CHEMICAL CO)
22 March 1996 (1995-03-22)

Y page 1, line 9-15 - line 53-57

page 3, line 3,4 - line 19,20

claim 1

1,11,15

1-7,11,13-15

claim 1

1,11,15

1-7,11,13-15

claim 1

1,11,15

1-7,11,13-15

claim 1

1,11,15

1-7,11,13-15

claim 1

1,11,15

1-7,11,13-15

claim 1

1,11,15

1-7,11,13-15

claim 1

1,11,15

1-7,11,13-15

claim 1

1,11,15

1-7,11,13-15

claim 1

1,11,15

1-7,11,13-15

claim 1

1,11,15

1-7,11,13-15

claim 1

1,11,15

1-7,11,13-15

claim 1

1,11,15

1-7,11,13-15

claim 1

1,11,15

1-7,11,13-15

claim 1

1,11,15

1-7,11,13-15

claim 1

1,11,15

1-7,11,13-15

claim 1

1,11,15

1-7,11,13-15

claim 1

1,11,15

1-7,11,13-15

claim 1

Form 99/00776
Form 99/00776

	(Continuation) DOCUMENTARY COMPRISED OF TWO SEPARATE PAGES	(Reference to other No.)
	Category - Citation of document, with indication where relevant, of the relevant passages	
Y	HP 98 27117 A (RESERAR ARIE CONNELLS : TWO (NL); THORNTON JEFFREY W. (NL)) 25 June 1998 (1998-06-25) cited in the application page 1 pages 3-4 page 5, line 1-5, 16-30 page 6, line 16 page 7, line 1, 2 - line 27-29 page 13, line 1, 2 - line 21, 22	1-7, 11, 13-15
X.P	CORTELLI T ET AL.: "A novel co-crosslinked polyacrylamide: studies for a controlled delivery matrix" JOURNAL OF CONTROLLED RELEASE, vol. 55, no. 1, 30 October 1994 (1994-10-30), page 57-66 XP004143500 page 1 page 3, column 1	1-3
A.P	EP 0 889 063 A (KAO CORP) 7 January 1999 (1999-01-07) page 3, line 23-29 page 4, line 16-20 page 5, line 10-30 page 8, line 4-9	1-3
A	US 5 371 208 A (KOZULIC BRANKO) 6 December 1994 (1994-12-06) page 1, column 11, column 17, line 3, 4 column 25, line 33-35	1, 7
A	US 4 582 865 A (BALLATS ERDINE A ET AL) 15 April 1986 (1986-04-15) column 1-2, line 35-40 column 4, line 35-46 column 12, line 35-46	1
A	EP 0 530 438 A (MUCHEST CELEANE CORP) 10 March 1993 (1993-03-10) page 3, line 1-23	1
A	EP 0 083 267 A (RHONE POULENC SA) 6 July 1983 (1983-07-06) page 9-11	1, 10

information on patient history, laboratory

Information on parent treaty members

Item: 2004 April/June 16
 PCT/NL 99/00776

Patent document class or action report	Publication date	Parent treaty member(s)	Publication date
EP 0044207 A	22-03-1995	US 6340132E D DE 6940132E T DE 6940132E T JP 718531 A JP 5396591 A US 5451613 A US 5462972 A	24-05-1994 1-02-1997 13-08-1997 25-07-1995 27-03-1995 19-09-1995 31-10-1995
WO 9827117 A	25-06-1998	AU 5346398 A EP 0946598 A	15-07-1998 06-10-1999
EP 0889063 A	07-01-1999	JP 288330 B	19-04-1999
US 5301208 A	06-12-1994	AT 184614 T CA 2112450 A DE 6932642 D EP 0604862 A EP 6316592 A US 5541255 A US 5767196 A	15-07-1999 01-10-1994 21-10-1999 06-07-1994 15-11-1994 30-07-1996 16-06-1998
US 4582865 A	15-04-1986	AU 4504585 A AU 572419 B AU 7217387 A CA 1230186 A DE 3520008 A DE 3546811 C FR 2574414 A GB 2169067 A, B GB 2181147 A, B GB 2181148 A, B GB 2205948 A, B IT 1187373 B IT 1745462 C JP 4030961 B JP 1915498 C JP 2138346 A JP 6037575 B SE 460792 B SE 8503466 A SE 501828 C SE 8901672 A SE 5128326 A US 4636524 A US 4605691 A	21-01-1986 12-01-1986 05-05-1988 27-08-1987 08-12-1987 19-05-1986 02-09-1993 13-05-1986 11-04-1986 15-04-1987 15-04-1987 25-12-1988 29-12-1987 25-03-1993 25-05-1992 26-06-1986 23-03-1995 28-05-1990 18-05-1994 20-11-1989 07-06-1986 22-05-1995 10-05-1989 07-07-1992 13-01-1987 12-08-1986
EP 0530438 A	10-03-1993	AT 148899 T CA 2065926 A DE 69217433 D DE 69217433 T DE 69217433 T DK 530438 T ES 2097235 T FI 921640 A GR 3022663 T MX 9201734 A NO 179590 B	15-02-1997 04-03-1993 27-03-1997 26-06-1997 18-08-1997 01-04-1997 04-03-1993 31-05-1997 01-03-1993 29-07-1996

INTERNATIONAL SEARCH REPORT

Patent document cited in search report			Publication date		Patent family member(s)		Date and Application No. PCT/NL 99/00776		Publication date	
EP 0530438	A				TR	26455 A			16-02-1994	
					US	5453323 A			26-09-1995	
EP 0083267	A		06-07-1983		FR	2519922 A			01-07-1983	
					AU	540455 B			09-04-1987	
					RU	219582 A			07-07-1983	
					BR	227847 A			26-10-1983	
					CA	1179314 A			18-12-1984	
					ES	518509 D			01-10-1983	
					ES	8308923 A			16-12-1983	
					CA	7389 A			31-08-1984	
					US	4755468 A			05-07-1988	

Form PCT/ISA/210 (Latest amended) (July 1992)

THIS PAGE BLANK (USPTO)

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

THIS PAGE BLANK (USPTO)